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Reductive Degradation of Dieldrin and Endrin in the Field Using Acidified Zinc

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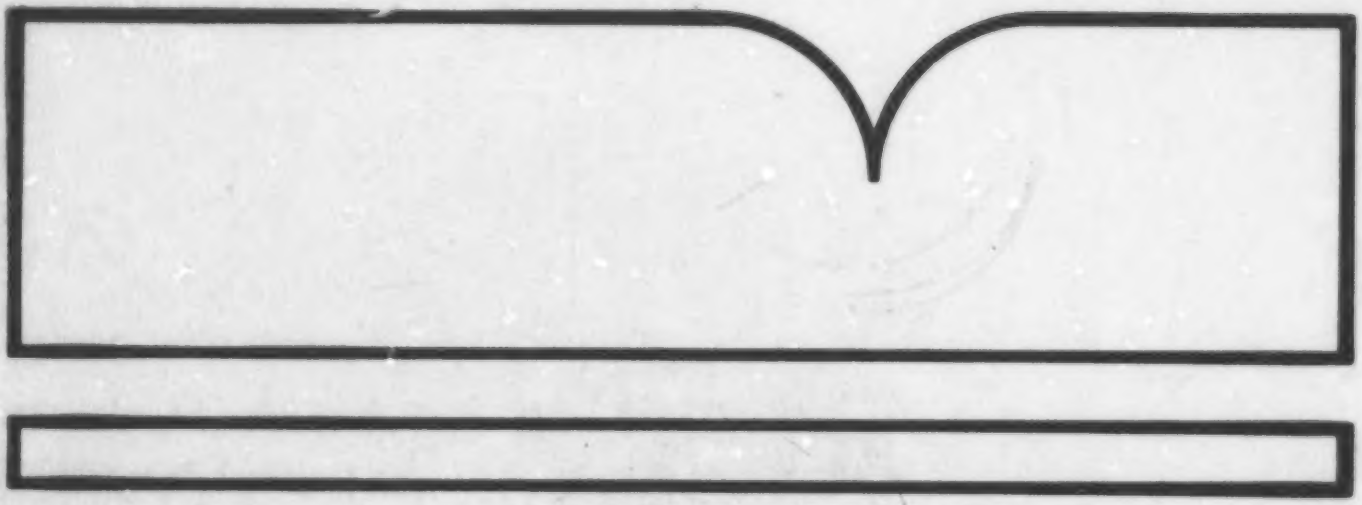

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REDUCTIVE DEGRADATION OF DIELDRIN AND ENDRIN IN THE FIELD USING ACIDIFIED ZINC

Key Words: Dieldrin, Endrin, Disposal, Insecticide, Persistence, Zinc, Soil

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ABSTRACT

The reductive dechlorination of dieldrin and endrin was investigated as a possible procedure for field disposal of small quantities of these pesticides. The objective was to convert the parent compounds to environmentally less objectionable materials. Emulsifiable concentrate formulations of the pesticides in a soil

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slurry were mixed with powdered zinc, dilute acetic acid, and acetone to facilitate reaction. Analysis of the mixtures by GC-MS indicated essentially complete conversion of endrin and partial conversion of dieldrin to products probably formed by replacement of the bridge anti chlorines with hydrogen. Partial confirmation of the desired anti dechlorodieldrin product was made by nmr. Disappearance of the parent compounds and production of conversion products was monitored for 2 1/2 years by GC in an outside soil plot, and accelerated destruction of parent compounds was achieved by the treatment. By analogy to the bridge anti dechloro products of aldrin and isodrin, the anti dechloro products probably are much less toxic than the parent compounds and are therefore environmentally less objectionable.

INTRODUCTION

The pesticides dieldrin (3,4,5,6,9,9-hexachloro-1aα, 2β, 2aα, 3β, 6β, 6aα, 7β, 7aα-octahydro-2,7:3,6-dimethanonaphth[2,3-b]oxirene) and endrin (3,4,5,6,9,9-hexachloro-1aα, 2β, 2aβ, 3α, 6α, 6aβ, 7β, 7aα-octahydro-2,7:3,6-dimethanonaphth[2,3-b]oxirene) are persistent in the environment,[1] highly toxic to wildlife[1] and carcinogenic.[2,3] These pesticides differ both in their ability to be accumulated and stored in vertebrate tissues and in their acute toxicity. Endrin is eliminated very rapidly from vertebrate tissues, but has a higher acute toxicity than dieldrin.[1] However, both dieldrin and endrin are similarly persistent in the soil with a normal half-life of about 6 years.[4,5]

In spite of the recent heavy restrictions on their use, there are still quantities of unused or outdated materials in storage on farms that will eventually need to be disposed of in a safe and environmentally acceptable manner. Because of the toxicity and environmental persistence of these two compounds, new means must be sought to bring about their degradation to less harmful compounds. Since disposal of small quantities of pesticides by open field burial may be permitted,[6] a practical and economical means for the reductive degradation of such concentrated formulations of unused dieldrin and endrin are needed to reduce the hazard to human health. Earlier studies by this laboratory have shown that the addition of powdered zinc in an acidic medium to DDT,[7] and to methyl parathion[8] during disposal by burial is a practical means for degrading small quantities of these pesticides. The purpose of this study was to determine if, under field conditions, this reaction would also accelerate degradation of dieldrin and/or endrin to breakdown products which were less toxic and more environmentally acceptable than the parent compounds. Test plots were monitored for 2 1/2 years to determine if there were further changes of the breakdown products during an extended period of time.

MATERIALS AND METHODS

The experiment involved mixing soil, emulsifiable concentrate (E.C.) dieldrin or endrin, powdered zinc, dilute acetic acid and acetone to hasten pesticide degradation. Test plots in the field were formed by the method previously described.[7,8]

The amounts of zinc added were 1.3 moles, 2.6 moles, or 6.5 moles per 0.4 moles of either dieldrin or endrin active ingredient, resulting in molar ratios of zinc to dieldrin or endrin of 3.3, 6.5, and 16.3 respectively. Each treatment was replicated four times. After addition of zinc, the other reagents were added in the manner previously described [7,8] using 473 ml of either 17.9% E. C. dieldrin or 19.7% endrin. Controls, sampling methods, type of soil used, weather conditions to which the plots were subjected and extraction methods were also as previously described.[7,8]

Dieldrin residues were analyzed using a Varian 1527C Gas Chromatograph equipped with a 130 mc tritium electron capture detector (ECD). A glass column, 1.83 m x 3.7 mm, packed with 1.5% OV-17 on 100/120 mesh Chromosorb G, was used with a nitrogen carrier flow of 32 mL/min and a temperature of 200°C. Endrin residues were analyzed with a Tracor MT-220 Gas Chromatograph equipped with a 130 mc tritium ECD. A glass column,1.83 m x 3.7 mm, packed with 10% DC-200 on 80/100 mesh Gas Chrom Q,was used with a nitrogen flow of 100 mL/min and a temperature of 200°C.

Sample extracts from the reduction of dieldrin and endrin with 3.3 and 16.3 mole ratios of powdered zinc to pesticide were analyzed after a one year period by gas chromatography/mass spectrometry. A Hewlett Packard 5930A mass spectrometer, equipped with a Hewlett Packard 5933A data system and a 5700A gas chromatograph, was employed. The 1.83 m x 2.0 mm glass column was packed with 3% OV-17 on 100/120 mesh Gas Chrom Q, using a helium carrier flow of 42 mL/min and an isothermal temperature of 190°C, for dieldrin.

GC-MS conditions for endrin were identical, except that the GC column was packed with 1.5% OV-17/1.95% OV-210 on 80/100 mesh Gas Chrom Q.

Preparative gas chromatography for dieldrin only was carried out using a Tracor MT-220 Gas Chromatograph with a 130 mc tritium ECD which had a "homemade" capillary collection tube attached to the ECD exit port. Only the major degradation product of dieldrin was collected, requiring over 100 injections of 50 µl each to obtain about 100 µg of sample.

Further analysis of this major degradation product of dieldrin was by means of nuclear magnetic resonance (nmr) spectroscopy. The initial sample was dissolved in deuterochloroform and analyzed on a Brucker WH-90 nmr system. Later this same sample was evaporated and redissolved in acetone-d_6 for nmr spectroscopy on a Varian XL-100 with a Nicolet T-100 Fourier Transform System and a MONA Multinuclear Accessory.

RESULTS AND DISCUSSION

Table 1 shows that the acidified zinc treatment greatly decreased the initial concentration of dieldrin and endrin. The treatment was more effective with increasing amounts of zinc. The half-life of both dieldrin and endrin was reduced from its unassisted level of about 6 years[9] to about 0.5 year by the reaction, an approximate ten-fold increase in the rate of degradation. The data indicates that there was little or no further breakdown after one year. In addition to the disappearance of the parent compounds,

TABLE 1

Degradation of Dieldrin and Endrin in Soil Plots with Acidified Powdered Zinc, Acetone, and 10% Acetic Acid[a]

Treatment[b]	Dieldrin or endrin recovery (µg of soil) at different times after treatment.[c]					
	Initial		1 year		2 1/2 years	
	Dieldrin	Endrin	Dieldrin	Endrin	Dieldrin	Endrin
Blank control, 6.5 moles Zn	0	0	0	0	0	0
No Zn	32,074 ±1,274	28,500 ±2,110	2,100 ±265	6,500 ±1,410	1,880 ±95	5,400 ±1,260
1.3 moles Zn	15,800 ±750	5,750 ±437	2,410 ±237	447 ±54	1,580 ±139	331 ±87
2.6 moles Zn	12,600 ±1,020	8,600 ±1,410	1,810 ±340	212 ±61	2,290 ±162	299 ±68
6.5 moles Zn	9,340 ±417	2,320 ±677	1,750 ±305	997 ±712	1,800 ±165	1,150 ±655

[a] Experimental conditions are given in references 7 and 8.

[b] The blank controls contained no pesticide. All of the other treatments contained 0.4 mole pesticide.

[c] Mean ± standard error for 4 replicates.

the production of one or more conversion products was apparent, as can be seen in Figures 1A and B for dieldrin and 1C and D for endrin. As the amount of parent dieldrin decreased (relative retention time, rrt = 1.00) other products (rrt = 0.73 and 0.22) were observed to form and to continue to be formed with time. Similarly for endrin (rrt = 1.00), other products formed as endrin disappeared (rrt = 1.56, 0.84, 0.74 and 0.49). These estimates of the effectiveness of the various treatments were based on the assumption that each component's gas chromatographic response, as a percentage of the total response of all components in the sample, was an accurate estimate, or that the electron capture response of a pesticide and its conversion products are equal on a molar basis. Verification of this assumption would have required isolation and purification of each of the conversion products in quantities sufficient to determine their relative response. Using this assumption it appears from Figures 1A through D that the reactions were essentially complete after one year.

It was not practical to identify all the reaction products in the extracts from all of the powdered zinc-acetic acid reductions of dieldrin and endrin. However, analysis by gas chromatography/mass spectrometry of extracts from the 3.3 and 16.3 mole ratio acidified reductions after a one year period indicated the formation of the predicted conversion products, mono-anti-dechlorodieldrin, and mono-anti-dechloroendrin, and disclosed the probable formation of products formed by further removal of chlorine atoms, first from the syn positions and second from other positions in the

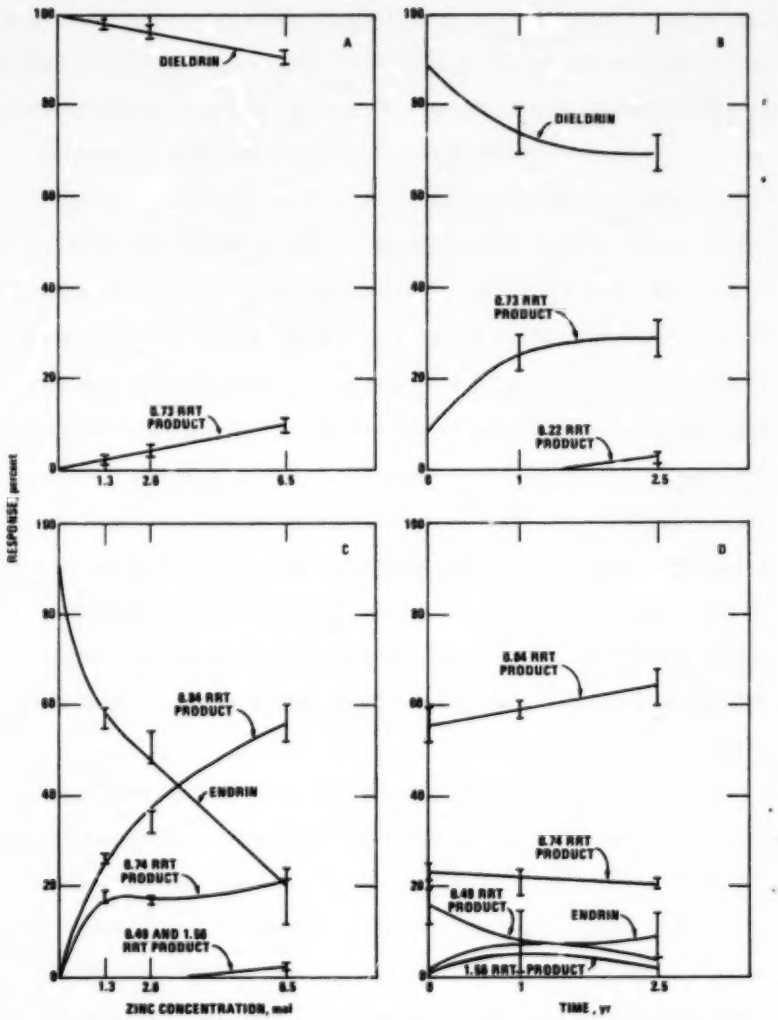

Fig. 1. Persistence of dieldrin and endrin in soil. A=initial effect of Zn concentration on dieldrin degradation; B=effect of time on dieldrin and its reaction products at the 6.5 mole Zn level; C=same as A, except endrin; D=same as B, except endrin. Experimental conditions are given under methods. Bars indicate ± standard error for 4 replicates.

molecule, as seen in Table 2. Priority loss of the anti-bridge chlorine atom in similar reactions has been shown frequently, for example in reductions with sodium borohydride,[10] or in acid treatment.[11] More stringent conditions using alkali metals in liquid ammonia caused complete degradation of dieldrin.[12] By analogy to known bicyclic systems,[13] where a π electron lobe in an anti-7-norbornenyl system lies on the side opposite to a bridge leaving group, it is likely that here too the anti halogen has been removed preferentially, with syn loss secondarily, followed by loss of other lower priority chlorines in the molecule.

Although the above were considered most likely conclusions, other products were also possible from the GC-MS results, which would be consistent with reasonable chemical transformations. Thus these results are not an absolute proof of the structures involved. Final identification and quantitation of these products would require independent synthesis of each compound with further chemical and instrumental analysis. However, in an attempt to offer further proof of structure, some of the major product was collected from a representative dieldrin field reduction by preparative gas chromatography. The tediousness of this procedure precluded collecting more than 100 µg of sample. Proton nmr spectra of the dechlorodieldrin product, summarized below and in Table 3, allowed elimination of structures (1) and (3) in Figure 2, and support, but do not conclusively prove, structure (2). No proton resonance was observed in the vinyl region, δ 4.6-8.7 in cyclic olefins, which rules out structure (1). The proton spectrum of

TABLE 2

Mass Spectral Data

Compound	RRT[a]	M^+(#Cl)[b]	Mass shift[c]	Assigned composition
Dieldrin				
-	0.13	None[d]	-	-
-	0.36	None[d]	-	-
Didechloro-dieldrin	0.46	310(4Cl)[d]	-68	$C_{12}H_{10}Cl_4O$
Monodechloro-dieldrin	0.72	344(5Cl)[e]	-34	$C_{12}H_9Cl_5O$
Dieldrin	1.00	378(6Cl)	0	$C_{12}H_8Cl_6O$
Endrin				
Didechloro-endrin	0.48	310(4Cl)[d]	-68	$C_{12}H_{10}Cl_4O$
Monodechloro-endrin	0.70	344(5Cl)[d]	-34	$C_{12}H_9Cl_5O$
Endrin	1.00	378(6Cl)	0	$C_{12}H_8Cl_6O$
Monodechloro-endrin	1.03	344(5Cl)[e]	-34	$C_{12}H_9Cl_5O$

[a]RRT is relative retention time, relative to standard dieldrin or endrin defined as 1.00 under the gas chromatographic conditions used in materials and methods.

[b]M^+ is the molecular ion.

[c]Mass shift from dieldrin or endrin.

[d]Minor product.

[e]Major product.

TABLE 3

Dieldrin Nuclear Magnetic Resonance Data

Unknown[a]		Dieldrin[b]		
δ	Mult., Integral	δ	Mult.	Asst.
4.04	s, 1H			
3.09	s, 2H	3.27	s, 2H	4,5
2.68	s, 2H	2.87	s, 2H	2,7
2.60	s, 2H	2.66	s, 2H	3,6
1.0[c]	AB	1.10	AB,2H[d]	12

[a] $CDCL_3$

[b] Acetone-d_6

[c] This region partially overlain by methyl resonance from GC column packing.

[d] J=13 Hz.

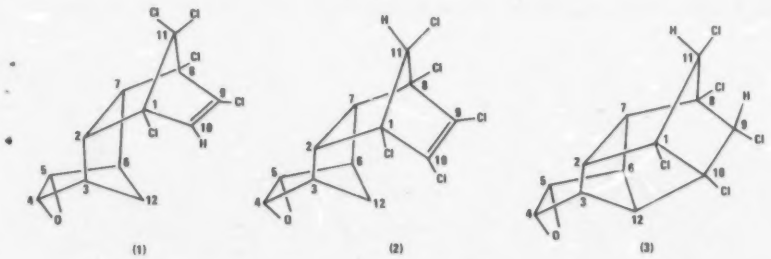

Fig. 2. Possible structures from GC-MS for monodechlorodieldrin, $C_{12}H_9Cl_5O$.

the unknown did not match that of an authentic sample of (3). Other characteristics of the ^{1}H nmr spectrum correspond to those of the dieldrin parent, with the addition of a resonance at δ 4.04. This δ value is characteristic of a bridge CHCl proton, and in similar compounds[14] corresponds to a proton with a CH bond orientation anti to a double bond (δ_{syn} 4.4-4.7, δ_{anti} 4.0-4.1). Additionally, the 0.2 ppm increase in shielding of H-2 and H-7 supports the anti orientation of the bridge proton. The ^{1}H nmr spectrum of the unknown corresponds closely to that of (2) reported in the literature.[15,16] Slight differences may be due to solvent effects.

Although actual toxicity data are not available for the dechlorinated conversion products from endrin and dieldrin prepared here, they are available for the anti-bridge dechlorinated conversion products of aldrin[17] and isodrin,[18] which are in vivo precursors of dieldrin[19] and endrin,[20] respectively. (See Figure 3.). Since the known compounds are less toxic,[17,18] it might be assumed

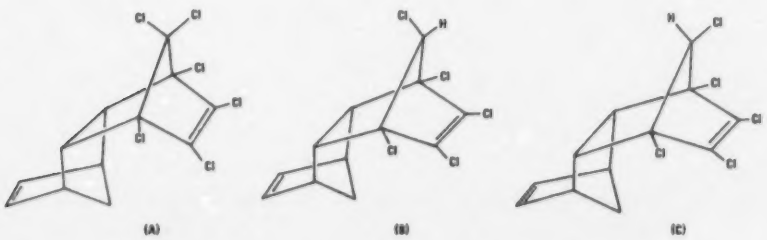

Fig. 3. Toxicity of analogs. A=aldrin, toxicity=100. B=Syn-dechloroaldrin, toxicity=8; C=anti-dechloroaldrin, toxicity=2.[17,18]

that the field reduction products are also less toxic by analogy. However, before degradation of dieldrin or endrin by this method can be recommended as a suitable field disposal procedure, the acute and chronic toxicities of the conversion products should be investigated.

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